

AD-A171 370

# FOREIGN TECHNOLOGY DIVISION



DTIC  
ELECTE  
SEP 03 1986  
S D

CARBON FIBERS

by

A.A. Konkin and N.F. Konnova



DTIC FILE COPY

Approved for public release;  
Distribution unlimited.

## PARTIALLY EDITED MACHINE TRANSLATION

FTD-ID(RS)T-0761-86

22 August 1986

MICROFICHE NR: FTD-86-C-002128

CARBON FIBERS

By: A.A. Konkin and N.F. Konnova

English pages: 30

Source: Zhurnal Vsesoyuznogo Khimicheskogo  
Obshchestva, Vol. 17, Nr. 6, 1972,  
pp. 632-639

Country of origin: USSR

This document is a machine translation.

Requester: AFWAL

Approved for public release; Distribution unlimited.

THIS TRANSLATION IS A RENDITION OF THE ORIGINAL FOREIGN TEXT WITHOUT ANY ANALYTICAL OR EDITORIAL COMMENT. STATEMENTS OR THEORIES ADVOCATED OR IMPLIED ARE THOSE OF THE SOURCE AND DO NOT NECESSARILY REFLECT THE POSITION OR OPINION OF THE FOREIGN TECHNOLOGY DIVISION.

PREPARED BY:

TRANSLATION DIVISION  
FOREIGN TECHNOLOGY DIVISION  
WPAFB, OHIO.

## MT TRANSLATION CORRECTIONS

As you use this document you may see technical translations which are incorrect or less than optimum. Translation Division personnel will be grateful for any corrections you forward to us. The next page contains blanks for your convenience in recommending better technical translations.

We need three things: the incorrect or poor translation, the correct or improved word or phrase, and the foreign page number.

Example:

Translation # FTD-ID(RS)T-0204-86 (Provided by SIT)

Foreign Page # \_\_\_\_\_

Incorrect word/phrase: \_\_\_\_\_

Recommendation: \_\_\_\_\_

Foreign page numbers occur in the English text and may be found anywhere along the left margin of the page as in this example:

In them occurs the state named "night blindness" - hemeralopia, which, according to the current point of view, is a result of damage of the rod-shaped apparatus of the eye.

Page 51.

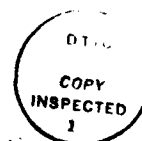
However, in recent years it has been shown that with the hereditary pigment degenerations in animals the biochemical changes are observed in all cellular elements of the retina.

Remove the sheet with your recommendations from the translation and forward it to:

SITR/Mr Koolbeck/76538

The dictionary modification process requires from six weeks to six months to accomplish; therefore it will be some time before the results of your recommendations will be evident in translations.

We thank you for your assistance in improving the machine translation product.



Dist	Special	or
A-1		

TRANSLATION # FTD-ID(RS)T-0761-86

Foreign Page # \_\_\_\_\_

Incorrect word/phrase: \_\_\_\_\_

\_\_\_\_\_

Recommendation: \_\_\_\_\_

\_\_\_\_\_

Foreign Page # \_\_\_\_\_

Incorrect word/phrase: \_\_\_\_\_

\_\_\_\_\_

Recommendation: \_\_\_\_\_

\_\_\_\_\_

Foreign Page # \_\_\_\_\_

Incorrect word/phrase: \_\_\_\_\_

\_\_\_\_\_

Recommendation: \_\_\_\_\_

\_\_\_\_\_

Foreign Page # \_\_\_\_\_

Incorrect word/phrase: \_\_\_\_\_

\_\_\_\_\_

Recommendation: \_\_\_\_\_

\_\_\_\_\_

# U. S. BOARD ON GEOGRAPHIC NAMES transliteration SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

\*ye initially, after vowels, and after ъ, ь; e elsewhere.  
When written as ё in Russian, transliterate as yě or ě.

## RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	sinh <sup>-1</sup>
cos	cos	ch	cosh	arc ch	cosh <sup>-1</sup>
tg	tan	th	tanh	arc th	tanh <sup>-1</sup>
ctg	cot	cth	coth	arc cth	coth <sup>-1</sup>
sec	sec	sch	sech	arc sch	sech <sup>-1</sup>
cosec	csc	csch	csch	arc csch	csch <sup>-1</sup>

Russian English

rot curl  
lg log

## GRAPHICS DISCLAIMER

All figures, graphics, tables, equations, etc. merged into this translation were extracted from the best quality copy available.

Page 632.

#### CARBON FIBERS.

Professor A. A. Konkin, Candidate of Technical Sciences N. F. Konnova.

In connection with development of missile construction, aircraft construction, mastery/adooption of space, and also other branches of technology arose sharp/acute need for high-temperature (oxidation-resistant) fibrous materials, reinforced plastics on basis of which were intended for exploitation at high temperatures. Common natural and synthetic fibers, including thermoresistant, could not satisfy these requirements.

As a result of intensive investigations, carried out for latter by decade are developed methods of obtaining large number of high-temperature (oxidation-resistant) fibers different in properties, predominantly on basis of inorganic compounds. To the important of them relate carbonic/carbon, boric, carbide, metallic, on the basis of oxides of the elements and some other compounds. Filamentary crystals (whiskers) occupy special position in view of unique mechanical properties. This group of fibers is located on different level of technical development. Some of them are produced on the industrial scale, others - in the experimental the third did not leave beyond the framework of laboratory investigations.

Among high-temperature (oxidation-resistant) fibers to volumes of production carbon and boron fibers occupy leadership in. On the high-temperature (oxidation-resistant) fibers there is a vast scientific-technical literature, to examine which within the framework of this survey on is possible. Taking into account this fact, this article is dedicated to carbon fibers. Brief information about other high-temperature (oxidation-resistant) fibers is given in the monographs <sup>1</sup>.

Source material and requirements for it.

Carbon fibers were for the first time obtained by Edison as early as 1888. The synthetic fibers, obtained from the cotton cellulose, served as source material. These carbon fibers long time were used in the electric lamps of heating. with the advent of tungsten filaments carbon fibers lost their value. Only in the last 15 years interest in them again revived, and in this direction intensive investigations began to be conducted.

All forms it is potentially possibly of raw material, used for obtaining carbon fibers, it is possible to subdivide into two groups: 1) chemical and natural fibers, 2) some polymers, mixture of organic compounds with high carbon content (petroleum pitch, coal tars), lignin, etc. Substances of the second group, independent of their chemical nature, initially are converted into the fibers, which then are treated into carbon fiber materials. Thus, in both cases as

initial material serve fibers, since only on the basis of the compounds, which have the form of fiber, it is possible to obtain carbon fibers of analogous form.

Principle of method consists in the fact that organic fibers in strictly controlled/inspected conditions undergo thermal breakdown, as a result of which is accomplished/realized transition from organic to carbon fiber. Process consists of two basic stages: carbonation (during 900-1500 °C) and graphitizations (with 1500-3000 °C ). Respectively fibers are subdivided into the carbonic/carbon and the graphite.

Fibers, intended for treatment/processing into carbonic/carbon materials, must satisfy the following basic requirements: not to be melted in process of carbonation; to give high output/yield of carbon fiber; to provide obtaining carbon fiber with high physicomechanical indices.

First two requirements are obvious. If fiber is melted during the carbonation, then it is impossible to keep the fibrous form of material. Nonmelting must be not only initial fibers, but also intermediate products of thermal decomposition of polymer. The possibility of applying the fusing fibers is not eliminated, but in this case is produced their preliminary processing/treatment, predominantly the oxidation, which leads to the loss of the meltability of polymer. The high yield of carbon is dictated by



technical economic consideration, since the cost of carbon fibers is sufficiently high. The properties of carbon fiber are determined by the structure of the transitional forms of carbon, which, in turn, depends on chemical nature of initial fiber, character of the intermediate products of thermal decomposition, conditions for carbonation and graphitization, and also on other factors.

Almost all known types of chemical and natural fibers were subject of investigation. However, for a number of reasons practical use find polyacrylonitrile fiber (PAN) and viscose cord fiber, on basis of which are organized industrial productions of different types of carbon fibers.

Obtaining carbon fibers from PAN and hydrated cellulose fiber.

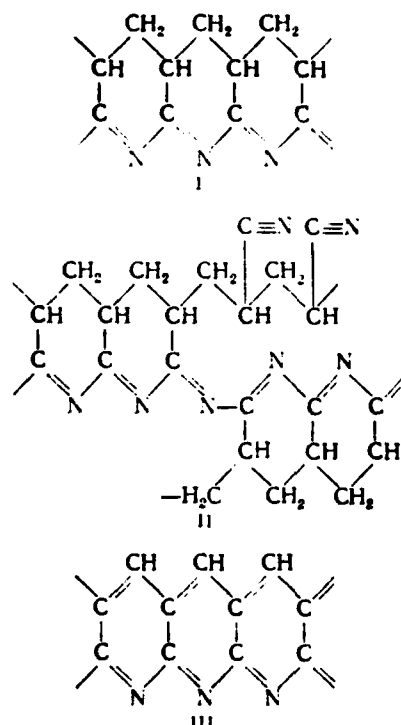
According to data of work<sup>[1,2]</sup> for obtaining carbon fiber on basis of PAN it is possible to use fiber with common strength (on the order of 35-40 kg/mm<sup>2</sup>); however, in other works<sup>[3,4]</sup> straight/direct interrelation between the mechanical properties of initial and carbon fibers (Fig. 1) is established/installed.

During utilization of PAN-fibers most critical is stage of oxidation.

Page 633.

During the thermal oxidation the cyclization with the formation of

stairs polymer and the addition/connection of oxygen to the polymer occurs, which covers the subsequent dehydrogenation of PAN. Is proposed a large number of diagrams of cyclization, but, apparently, most reliable is the diagram of Grassi and coworkers[5], according to which are formed naphthyridine cycles (I), molecular bonds (II), also, under the more rigorous conditions of heating aromatic heterocycles (III):



Cyclization of PAN is confirmed by many researchers, and kinetics of this process during utilization of method of IKS is studied by authors of work[6]. The formation of intermolecular bonds indicates an increase in the viscosity of the solution and reduction in the solubility of oxidized PAN[7]. It is known that the alkalis, amines, amides of alkali metals, nucleophilic reagents and other compounds

catalyze cyclization<sup>[1,2-10]</sup>. The regularity of the construction of chain also contributes to cyclization. The majority of researchers adheres to presentation/concept about the chain mechanism of cyclization of PAN<sup>[1, 2, 3, 4]</sup>

In scientific literature and in patents are given different regimes of oxidation of PAN-fiber<sup>[13]</sup>: duration of 1-44 h at 200-300°C. On the process of obtaining the high-strength fiber to that developed in England, is recommended the following regime of oxidation<sup>[14]</sup>: the duration of 24 h at 220°C.

Important role plays drawing of fiber during oxidation<sup>[14]</sup>. During the oxidation in the free state the fiber undergoes contraction with the simultaneous disorientation of the structural elements. Drawing leads to a significant increase in strength and Young's modulus carbon and graphite fiber. The effect of drawing on Young's modulus graphite fiber is shown in Fig. 2. Only because of this technological procedure it was possible to obtain high quality carbon fibers. However, during the utilization of high-strength (67-80 rkm) PAN-fiber oxidation is recommended to carry out under the conditions of the partial (10-15%) contraction of fiber<sup>[14]</sup>

In process of carbonation, which is conducted in inert atmosphere at 900-1500°C, occur deep chemical transformations and is accomplished/realized transition to carbon fiber. Carbonation is accompanied by the decrease in weight<sup>[15]</sup>, is most which intensively

occurs in region of 280-420°C, and by the contraction of fiber. The basic products of decomposition are HCN, NH<sub>3</sub>, H<sub>2</sub>O, besides this a large quantity of different products<sup>[1,2]</sup> is separated/liberated.

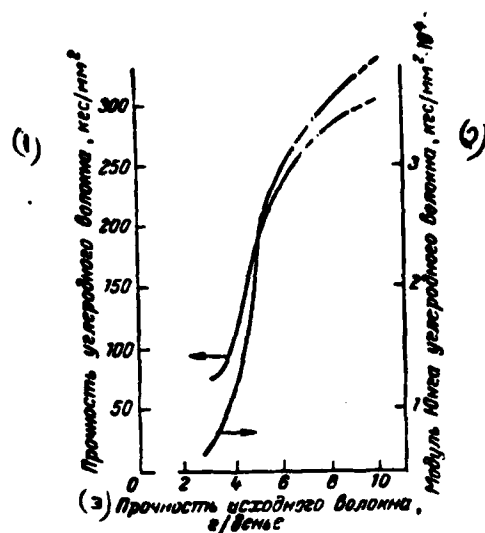


Fig. 1. Effect of strength of initial PAN-fiber on strength and Young's modulus carbon fiber[4]

Key: (1). Strength of carbon fiber,  $\text{kgf/mm}^2$ . (2). Young's modulus of carbon fiber,  $\text{kgf/mm}^2 \cdot 10^4$ . (3). Strength of initial fiber, g/denier.

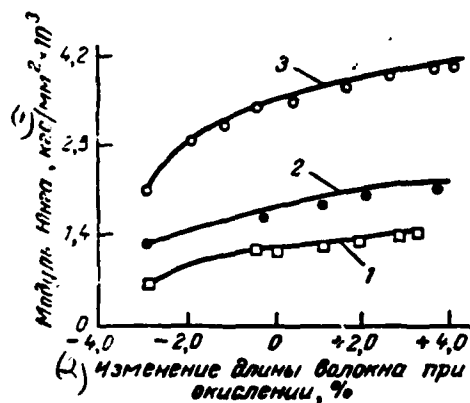


Fig. 2. Dependence of Young's modulus of carbon fiber on basis PAN on value of drawing during oxidation and temperature of subsequent processing/treatment: 1 - at 1000°C; 2 - 1500°C; 3 - 2500°C.

Key: (1). Young's modulus,  $\text{kgf/mm}^2 \cdot 10^3$ . (2). Change in fiber length with oxidation, %.

Page 634.

Remainder/residue is gradually enriched in carbon. It is characteristic that even at a final temperature of carbonation of 1000°C in the fiber it is contained by 8-10% of nitrogen. This it indicates that nitrogen enters into conjugated system of bonds, probably, cyclic structure.

In process of carbonation physical structure of polymer is changed. The structure of initial fiber disappears at 300°C. Aromatization of carbon<sup>[1,2]</sup> begins already at the early stage of the heat treatment (higher than 300°C), which the stairs structure of oxidized PAN favors. At a temperature of ~800°C or above occurs the aggregation of aromatic planes with the formation of the disordered structure of carbon.

They deserve attention of investigations, in which it is shown<sup>[1,2]</sup> that in process of carbonation, at least at its early stages, is retained initial fibrillar structure of polymer. Hence it follows that the physicochemical processes of destruction of polymer and the formation of carbonic/carbon skeleton occur in the limits of separate fibrils and as the result of this, that the fibrillar structure of the initial fiber cannot have effect on the properties of carbon fiber.

In accordance with physicochemical processes and with structural conversions are changed properties of fiber. As a result of polymer

destruction initially is observed the incidence/drop in the strength of fiber, which reaches minimum value approximately at 250-300°C and it corresponds to the maximum decrease in weight of polymer, then in proportion to an increase in the temperature of carbonation strength begins to increase/grow (Fig. 3). Young modulus of fiber analogously is changed. The increase of the mechanical properties of fiber coincides since the beginning of the formation of the two-dimensional graphite-like structures of carbon.

Upon transfer from PAN-fiber to carbonic/carbon three zones of change in electrophysical properties clearly are developed. initial fiber - typical dielectric; in the process of carbonation occurs the sharp decrease of electrical resistance and fiber acquires semiconductor properties, which in turn indicates the appearance of a high concentration of  $\pi$ -conjugations; and, finally, conductivity.

In the literature, especially in patents, are given different parameters of process of carbonation. The final temperature of carbonation lies/rests within limits of 800-1500°C, rate of climb of temperature of 0.5-0.3°C / h (see [1, 2]), the duration of processing/treatment 0.5-4 h. it is noted that the slow regimes of heating provide obtaining more high-quality fiber [1, 2]

Substantiated data about effect of drawing in process of carbonation on properties of fiber in literature is not brought. According to the series/number of patents, conducting process on rigid

framework/body gives possibility to obtain the high-strength carbon fiber (strength to  $300 \text{ kg/mm}^2$  and Young's modulus  $25 \times 10^3 \text{ kgf/mm}^2$ ).

At stage of graphitization most important of chemical transformations is splitting of nitrogen in the form  $\text{NH}_3$  and enrichment of remainder/residue carbon. As a result of graphitization is obtained the fiber, the carbon content in which is higher than 99%. The significant role play the physical processes, which are accompanied by the transformation of the hybrid forms ( $\text{sp}^1$ ,  $\text{sp}^2$ ,  $\text{sp}^3$ , . . .) of carbon, by an increase in the sizes/dimensions of crystallites (Fig. 4), by the decrease of the intermolecular distance of  $d_{001}$ , and increase of orientation and density of fiber. The strength of fiber is increased with an increase in processing/treatment temperature to  $1200\text{--}1500^\circ\text{C}$ , and then begins to be decreased (Table 1) Young's modulus continuously increases/grows. As a result of graphitization high- modulus carbon fiber (modulus/module  $35 \times 10^3\text{--}40 \times 10^3 \text{ kg/mm}^2$ ) with the average/mean strength  $200 \text{ kg/mm}^2$  is obtained. In the patent [10] are cited the data, according to which conducting graphitization under the tension makes it possible to increase simultaneously strength and initial modulus of fiber. Since the graphitization is conducted at high temperatures (to  $2500\text{--}2800^\circ\text{C}$ ), stringent requirements on the protective medium (argon) in the oxygen content are imposed. Duration of graphitization composes several minutes.

Obtaining carbon fiber from hydrated cellulose is composed of



three stages: preparation of initial fiber, carbonation and graphitization.

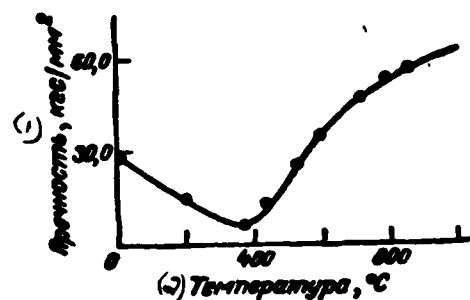


Fig. 3. Dependence of strength of fiber on temperature of carbonation<sup>[1,2]</sup>

Key: (1). Strength, kg/mm<sup>2</sup>. (2). Temperature, °C.

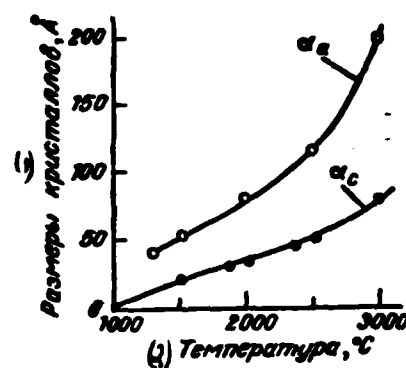


Fig. 4. Increase of sizes/dimensions of crystallites in dependence on temperature of graphitization<sup>[1,2]</sup>

Key: (1). Sizes/dimensions of crystals, Å. (2). Temperature, °C.

Page 635.

Preliminary preparation of fiber (cloth) is reduced to removal from it of organic impurities (lubricants) by processing/treatment by organic solvents<sup>[1,2]</sup>

In process of carbonation thermal breakdown of cellulose, which

is accompanied by numerous complex chemical reactions and structural transformations, occurs. To the process of carbonation, property of intermediate products and in the end carbon fibers influence many factors, and namely: catalyzers, temperature-time regimes, character of medium, property of source material and others. <sup>41</sup> The thermal breakdown of hydrated cellulose with the intensive decrease in weight is observed in the relatively narrow temperature range, which lie within the limits of 250-300 °C. As a result of destruction are formed volatile compounds (predominantly H<sub>2</sub>O, CO<sub>2</sub>, CO), resins and carbon remainder/residue<sup>[14]</sup>. A number of decay products is very great.

One of important levoglucosans<sup>[12]</sup> which is one of sources of formation of resins, relates.

Main reactions of thermal decomposition of cellulose include dehydration, depolymerization and strictly destruction, which is accompanied by deep decomposition of polymer and by formation of numerous low-molecular compounds. Dehydration and depolymerization are competing reactions, the relationship/ratio of speeds of which determines the yield of carbon. Because of the fact that dehydration begins at lower temperatures (on the order of 190°C) in comparison with depolymerization (250°C) it is possible to achieve a comparatively high yield of carbon from the cellulose.

Very great is the role of catalysts with pyrolysis. As the

catalysts are used the fireproofing compounds, acids and bases/roots of Lewis, salt of the metals of variable/alternating valence and others<sup>[23]</sup> The effect of the effect/action of catalysts appears in an increase in the output/yield of the carbon-containing remainder/residue (pitch) and of the gaseous products, the decrease of a quantity of resins and levoglucosan. Furthermore, in the presence of catalysts the decomposition of cellulose begins at lower temperatures and occurs in the wider temperature range. In the presence of catalysts during the first stage of heat treatment dehydration of cellulose more intensively flows/occurs and the reactions, which lead to the formation of tarry products, are depressed thereby.

Destruction of hydrated cellulose is accompanied by large number of reactions, which proceed according to homolytic and heterolytic mechanisms. It is possible to note two different approaches to the study of the mechanism of the decomposition of cellulose. The majority of researchers considers that as a result of dehydration the molecular bonds<sup>[24, 25]</sup> are formed, in the opinion whereas of Bacon<sup>[26]</sup>, it flows/occurs as intramolecular reaction. The first point of view is more probable, since because of the molecular bonds the form of fiber is retained.

In proportion to increase in temperature occurs enrichment of pitch by carbon with simultaneous removal/distance of other elements, in this case structure of pitch becomes complicated due to diversity

of transitional forms of carbon and large number of possible types of bonds between carbon atoms.

Thermal breakdown of cellulose is accompanied by structural transformations. At 250-350°C the complete amorphization of cellulose occurs. According to<sup>[11]</sup> aromatization of carbon begins at 240-270°C, and the phase of two-dimensional ordering of carbon, according to Fialkov and colleagues<sup>[12]</sup> appears at 300-400°C. The three-dimensional ordering (turbostratic structure), recorded by the reflection of X-rays, is revealed after heating at 900°C.

In process of carbonation are changed properties fiber. Qualitative picture is analogous to a change in the properties of PAN-fiber. Strength and modulus/module initially are decreased, understanding minimum value at 300°C, and then they increase/grow.

Carbonation of cellulose is conducted in protective medium, as which can be used nitrogen, decay products of cellulose, hydrocarbons, carbon filling and others<sup>[13]</sup>. Carbonation is accomplished/realized with slow, especially during the first stage, strictly adjustable temperature rise. To 300-400°C is recommended the raising of temperature with a velocity of 5-10°C / h, and then with speed of 60-100°C / h (see <sup>[30]</sup>). According to patent<sup>11</sup> total time of carbonation is 230-250 h.

Process of graphitization<sup>[14]</sup> is accomplished/realized during very

which time; rate of climb of temperature composes 1000-3000°C / h. At the stage of graphitization the improvement of the structure of carbon (increase in the sizes/dimensions of crystals, their orientation along the fiber axis, the decrease of interplanar spacing and, as a rule, an increase in fiber density) occurs<sup>[11,12]</sup> and respectively are increased strength and Young's modulus fiber, these indices continuously increasing/growing<sup>[32]</sup> with an increase in graphitization temperature.

Drawing exerts a substantial influence on orientation and mechanical properties of carbon fiber<sup>[11,12]</sup>. As a result of the drawing, conducted on the stages of carbonation and graphitization, are raised strength and Young's modulus of carbonized and graphitized fibers (Fig. 5).

Table 1. The temperature effect of processing/treatment on the properties of angular-native fiber[1.1]

(1) Температура, °C (продолжительность обработки 1 ч)	(2) Прочность, кг/мм <sup>2</sup>	(3) Модуль Юнга, кг/мм <sup>2</sup> × 10 <sup>3</sup>
1000	147,5	16,5
1500	225,0	24,6
2000	189,8	32,3
2500	179,3	38,7
2800	178,6	42,2

Key: (1). Temperatures, °C (duration of processing/treatment 1 h).

(2). Strength kg/mm<sup>2</sup>. (3). Young's modulus, kg/mm<sup>2</sup> × 10<sup>3</sup>.

Page 636.

Only because of the application drawing was possible to obtain carbon fibers possessing the very high mechanical properties (strength 200-300 kg/mm<sup>2</sup>, Young's modulus 25·10<sup>3</sup>-50·10<sup>3</sup> kg/mm<sup>2</sup>).

Other types of synthetic fibers.

Besides PAN-fiber and rayon tire cord, as subjects of investigation served many synthetic fibers: polyvinyl alcohol (PVS), Saran (copolymer of polyvinyl chloride and polyvinylidene chloride), polyethylene, polyamide, polyester, heterocyclic. However, to the systematic study were subjected PVS and Saran fiber.

Since majority of enumerated fibers is melted during heating, then is produced their preliminary oxidation, during which in polymer intermolecular chemical bonds are formed and it changes into

nonmelting state. One should note that from the types of synthetic fibers enumerated above thus far it was impossible to obtain high quality of carbon fibers.

According to patents<sup>[1,2]</sup> by oxidation of PVS-fiber at 200°C for 16 h and by subsequent carbonation and graphitization obtained carbon fiber by strength 62 kg/mm<sup>2</sup>. Via preliminary dehydrogenation of polymer<sup>[3,4]</sup> with the subsequent oxidation, carbonization and graphitization it was possible to obtain fiber by strength to 90 kgf/mm<sup>2</sup>.

From fiber Saran<sup>1</sup> in process of prolonged oxidation (15 h) at 140 and 190°C and carbonation was obtained carbon fiber, although with low mechanical properties (strength 34 kgf/mm<sup>2</sup>, Young's modulus 2800 kgf/mm<sup>2</sup>), having very large free surface (700-1000 m<sup>2</sup>/g. This fiber can serve as excellent sorbent. During the subsequent graphitization the mechanical properties of fiber little are changed, but free surface due to the stoppering of pores is reduced to 8 m<sup>2</sup>/g with the simultaneous decrease of density.

As subjects of investigation served aromatic and aliphatic polyamides<sup>[5,6]</sup> (nylon, nylon 6T, Nomex), aromatic polyesters/polyethers<sup>[7,8]</sup>, heterocyclic compounds (benzimidazoles, oxydiazoles)<sup>[9]</sup>. The principle of obtaining carbon fibers from the enumerated polymers is similar to the principle of obtaining carbon fiber of PAN consists of three stages - oxidation, carbonation and graphitization.



Oxidation of fibers conducted during long time at 200-300°C for polyamides and polyesters/polyethers and 450-475°C for fibers from heterocyclic compounds. However, to obtain high quality carbon fiber from these types of fibers thus far did not succeed.

Obtaining carbon fibers on basis is pitch.

It is established<sup>[3,7]</sup> that as a result of dehydrochlorination of PVC (with 390-450°C) in nitrogen atmosphere is obtained resin (pitch), possessing fiber-forming properties. Later on the basis of PVC-pitch was developed the process of obtaining the carbon fiber<sup>[4,8]</sup> known by the name MR-fiber.

Obtaining carbon fiber from pitch is made up of the following operations: spinning, its oxidation, carbonation, graphitization.

Initial material can serve as petroleum it baked and coal-tar pitch, from which preliminarily are removed volatile products. In Japan<sup>[4,9]</sup> is organized the production of carbon fiber from the petroleum pitch by the power on the order of 120 t/year.

Molding of fiber is most complex stage of technological process. Pitches are the mixture of oligomers (molecular weight 770-1100) with the low melting viscosity, molding of fiber from which with the required value of diameter of filaments (10-50  $\mu$ ) is connected with a number of difficulties. The temperature of molding for PVC-pitch composes 250-290°C, petroleum<sup>[4,8]</sup> of 260-300°C and coal-tar pitch<sup>[4,10]</sup> on

the order of 260°C.

For purpose of translation/conversion into nonmelting state[44] oxidation of fiber by atmospheric oxygen with ozone at temperature to 260°C is produced. For obtaining the high quality fiber during the utilization it is pitch necessary to conduct drawing in the process of carbonation and especially at the stage of graphitization. MR-fibers are obtained with strength 275 kg/mm<sup>2</sup> and Young's modulus 4800 kg/mm<sup>2</sup>. For this fiber the combination of high strength with the low modulus/module is characteristic.

Recently Canadian researchers[45] using high extracts at stage of graphitization (180%), from petroleum pitch obtained carbon fiber with strength 260 kg/mm<sup>2</sup> and Young's modulus 44000-63000 kg/mm<sup>2</sup>.

According to structure this type of fibers relates to glass-carbon[46] (to amorphous carbon). It also differs from the carbon fibers, obtained from PAN-fiber and the rayon tire cord, in terms of the absence of fibrillar structure.

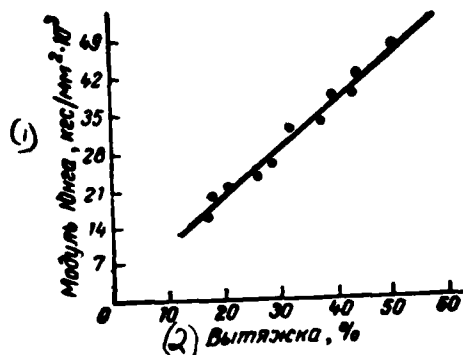


Fig. 5. Effect of drawing during graphitization on Young's modulus fiber. Temperature of graphitization of 2780- 2870°C, duration - 0.20-0.27 s.

Key: (1). Young's modulus,  $\text{kgf/mm}^2 \cdot 10^3$ . (2). Extract, %.

Page 637.

Obtaining of hydrocarbon fibers from phenol resins.

Thermal breakdown of phenolic resin in contrast to thermal destruction of majorities of polymers occurs in wide temperature range. This is caused by formation in the process of thermal decomposition of intermediate products with growing heat resistance; therefore their peculiar thermal stabilization occurs. With this, apparently, is connected the high output/yield of carbon fiber, which comprises to 65% of the weight of initial resin. Because of this specific property phenolic resin is the promising source of raw material for obtaining the carbon fiber.

Obtaining carbon fiber includes molding initial fiber, its solidification, carbonation, graphitization. As the source material the oligomers of the type of resol or novolaks<sup>[1,2]</sup> are used. Just as

during the utilization it is pitch, spinning is the most complex operation. Initial resin on the basis of some literary sources[<sup>11</sup>] must have molecular weight 185-367, on others[<sup>12</sup>]- 500-1200.

Solidification, necessary for obtaining of nonmelting fiber, can be achieved/reached by three means: processing of fiber by formaldehyde in presence HCl in liquid or vapor phase, by oxidation of fiber with heat treatment.

In the literature regimes of carboization are given. The character of a change of the strength of fiber in the dependence on the temperature of carbonation is shown in Fig. 6, from which it is evident that it continuously increases/grows up to 1000°C. Of this consists the peculiarity of the thermal breakdown of fibers of their phenolic resin in comparison with fibers, obtained from other polymers. As a result of carbonation carbon fiber[<sup>13</sup>] with strength 56-210 kgf/mm<sup>2</sup> and Young's modulus 3500-7000 kgf/mm<sup>2</sup> is obtained. According to the data of Economy[<sup>14</sup>] while conducting of graphitization under the tension it was possible to increase Young's modulus to 17150 kgf/mm<sup>2</sup>. Similar according to the structure to fibers from pitch, it relates to glass-carbon.

In comparison with petroleum (coal) pitch phenolic resin have series/number of advantages: synthesis of resins of simpler than preparation/training is pitch, they have more standard properties, thanks to which their treatment/processing is simplified, and, which

is especially important, they do not contain cancerogenic substances.

In connection with this phenolic resin should be considered as promising source of raw material for obtaining carbon fiber.

Properties and fields of application.

Carbon fibers similar to various forms of carbon and graphite possess valuable physicochemical properties. The at the same time inherent in carbon fibers specific form (fiber) and structure condition their unique mechanical properties.

Because of reticular structure and high concentration of  $\pi$ -conjugations carbon fibers have extremely high heat resistance and chemical inertness. Under the effect of the thermal effect the mechanical properties of fibers up to high temperatures are not reduced, but, conversely, they increase/grow [1].

Температура, °C	20	540	1100	1650
Прочность, кг/м ширины полосы	0,9—2,9	1,1—3,2	1,4—4,3	1,8—6,0

Key: (1). Temperature. (2). Strength, kg/m of bandwidth.

Carbon fibers are resistant to aggressive media, besides oxidizers; however, by application of carbides or other protective coatings it is possible to to a considerable extent remove this deficiency. Because of the high thermo- and the chemostability they are used for filtering of aggressive media and cleaning/decontamination of gases, preparation/manufacture of armored

clothing, as the heatproof means in the pure form or in the form of plastics. Unusually high ablation stability is also the characteristic and valuable property of plastics.

Changing parameters of process, it is possible to obtain fibers with different electrophysical properties (specific resistance of  $0.002-10^4 \Omega \cdot \text{cm}$ ), thanks to which they can be used as electrical heating elements (suits, heating of rooms, etc.), thermocouples, etc.

Carbon fiber can be obtained with very high surface area (to  $1000 \text{ m}^2/\text{g}$ ). Activation by water vapor makes it possible to sharply increase the free surface of carbon fiber, obtained from PAN<sup>[11]</sup> and celluloses. This fiber is excellent sorbent. Plotting on the fiber of catalysts makes it possible to create catalytic systems with the developed surface.

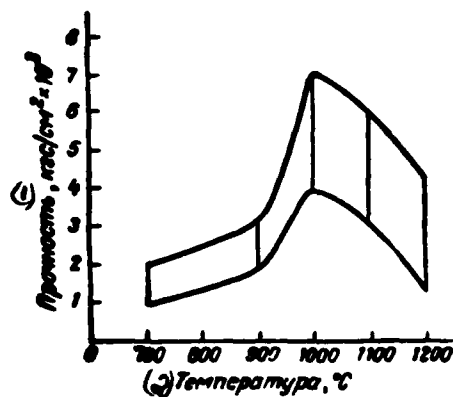


Fig. 6. Temperature effect of carbonation on strength of carbon fiber. Conditions of the carbonation: rate of climb of temperature  $0.7^{\circ}\text{C} / \text{min}$ , the diameter of fiber  $15\text{--}17 \mu$ .

Key: (1). Strength,  $\text{kg}/\text{cm}^2 \times 10^3$ . (2). Temperature,  $^{\circ}\text{C}$ .

Page 638.

Carbon fibers are obtained with different mechanical properties. To the fibers, intended for the utilization as the heatproof, filtering, sorption, electrically conducting materials, are not imposed stringent requirements on the mechanical characteristics. Fibers of the designation/purpose indicated have strength on the order of  $50\text{--}100 \text{ kgf}/\text{mm}^2$  and Young's modulus  $2000\text{--}7000 \text{ kgf}/\text{mm}^2$ .

In recent years methods of obtaining carbon fibers with unique mechanical properties, which, taking into account low density ( $1.6\text{--}2.0 \text{ g}/\text{cm}^3$ ), in terms of specific value of strength and Young's modulus exceed all known high-temperature (oxidation-resistant) fiber materials, are developed.

Strength of fibers is within the limits of 120-300 kgf/mm<sup>2</sup> and Young's modulus  $17.5 \cdot 10^3$ - $70 \cdot 10^3$  kgf/mm<sup>2</sup>. Comparative mechanical properties with the stretching of the epoxy-carbon plastics and other structural materials are given in Table 3. From these data it is evident that on the specific strength and the hardness the epoxy-carbon plastics exceed all most widely used structural materials. So/such high mechanical indices predetermine the possibility of the wide application of carbon-fiber reinforced plastics as the structural materials in different branches of technology.

One should note also that introduction of fiber to polymers conducts to increase in stability to abrasion of plastics by 1-2 orders, which makes it possible to increase service life of articles.



Table 2. Properties of high-strength high-modulus carbon fibers.

(1) Показатели	(2) Марки волокон (США) <sup>40</sup>							(3) Марки волокон (Англия) <sup>51</sup>	
	Торнель-25	Торнель-40	Торнель-50	Торнель-60	Торнель-70	Торнель-75	Торнель-100	Тип I	Тип II
(4) Модуль упругости, кг/мм <sup>2</sup> · 10 <sup>3</sup>	17,5	28	35	42	49	52,5	70,3	38—45	24,5
(7) Прочность, кг/мм <sup>2</sup>	126	170	200	227	227	240—260	352	145—210	280—315
(8) Плотность, г/см <sup>3</sup>	1,42	1,56	1,63	1,7	—	1,86	—	2,0	1,74
(9) Диаметр, мк	7,3	6,8	6,6	6,1	—	—	9,4	7,8	8,1
(10) Форма поперечного разреза	Изрезанная							Круглая	

Key: (1). Indices. (2). Brands/marks of fiber (USA) [50]. (3). Brands/marks of fiber (England) [51]. (4). Thornel. (5). Type. (6). Modulus of elasticity, kg/mm<sup>2</sup> · 10<sup>3</sup>. (7). Strength, kg/mm<sup>2</sup>. (8). Density, g/cm<sup>3</sup>. (9). Diameter, μ. (10). Form of cross section. (11). Cut. (12). Circular.

Table 3. Properties of epoxy-carbon plastics and other structural materials [53].

(1) Материал	(2) Плотность (γ), г/см <sup>3</sup>	(3) Прочность (σ), кг/мм <sup>2</sup>	(4) Модуль Юнга (E), кг/мм <sup>2</sup> · 10 <sup>3</sup>	(5) Удельная прочность (σ/γ)	(6) Удельный модуль (E/γ) · 10 <sup>3</sup>
(7) Сталь Eh19	7,8	100	20,7	12,8	2,66
(8) Сплав алюминия HV 30WP	2,7	34,5	6,9	12,8	2,5
(9) Сплав титана ДТД 5173	4,5	93,1	11,0	26,0	2,45
(10) Эпоксигластопластики (S-стекло)	2,12	192,5	6,9	91,0	3,25
(11) Эпоксигластопластик	2,1	49,7	15,5	23,7	7,4
(12) Эпоксигластопластик					
(13) а) с высокопрочным волокном	1,6	131,0	17,2	82,2	10,8
(14) б) с высокопрочным волокном	1,7	56,0	20,4	33,0	12,0

Key: (1). Material. (2). Density (γ), g/cm<sup>3</sup>. (3). Strength (σ) kg/mm<sup>2</sup>. (4). Young's modulus (E), kg/mm<sup>2</sup> · 10<sup>3</sup>. (5). Specific strength (σ/γ). (6). Specific modulus (E/γ) · 10<sup>3</sup>. (7). Steel Eh19. (8). Alloy of aluminum HV 30WP. (9). Alloy of titanium DTD 5173. (10). Epoxy glass fiber reinforced plastics (S-glass). (11). Epoxy boron fiber reinforced plastic. (12). Epoxy carbon fiber reinforced plastic. (13). a) with high-modulus. (14). b) with the high-modulus fiber.

## REFERENCES.

1. Ц. Карролл-Порчинский, Материалы будущего, изд. «Химия», 1966; сб. «Конструкционные материалы волокнистого строения», под ред. И. Н. Фраппевича, изд. «Наукова думка», Киев, 1970; сб. «Современные композиционные материалы», под ред. Л. Браутмана, Р. Крока, изд. «Мир», 1969.
2. Y. E. Bailey, A. G. Clarke, Chem. Brit., 6, 484 (1970).
3. R. Moreton, Inter. Conf. on Carbon Fibres their Compossiter a. Applic., London, 1971, paper № 12.
4. Франц. пат. № 2066795, 1971.
5. N. Grassie, T. Neill, J. Chem. Soc., 1956, 3929; N. Grassie, N. Novel, J. Polymer Sci., 48, 79 (1960); N. Grassie, T. Neill, ibid., 39, 211 (1959); N. Grassie, N. Hay, T. Neill, ibid., 31, 205 (1958); N. Grassie, N. Hay, ibid., 36, 189 (1962).
6. J. Ноп, Н. Јп, J. Polymer Sci., Part B, 4, 721 (1965).
7. М. А. Гейдерих, Б. Э. Давыдов, Б. А. Крейцель, Изв. АН СССР, ОХН, 1965, 636; Миятичи Кадзуо, Окамахо Масоо, Катаяма Масатичи, Сэл'н Гакайси, 22, 538, 540 (1966); 23, 36 (1967).
8. J. Mc Cartney, Nat. Bur. Stand., 525, 123 (1953).
9. C. G. Overberger, H. Iuki, N. Itakawa, J. Polymer Sci., 45, 127 (1960).
10. Bull. Chem. Soc. Japan, 35, 1438 (1953).
11. N. Grassie, Хим. и технол. полимеров, № 7—8, 158 (1960).
12. W. Makschin, Faserf. u. Text., 20, 321 (1969).
13. Франц. пат. № 1541287, 1968; № 1556024, 1968; № 1501286, 1967; № 1430603, 1966.
14. W. Watt, W. Johnson, Polymer Preprints, 9, 1245 (1968).
15. З. С. Смуткина, в сб. «Структурная химия углерода и углей», изд. «Наука», 1969, стр. 201; В. В. Полуэктова, Г. Г. Цуринов, З. С. Смуткина, там же, стр. 207; З. С. Смуткина, Э. А. Пакшвер, Р. А. Полотовская, В. В. Полуэктова, М. Е. Казаков, там же, стр. 214.
16. С. Мадорский, Термическое разложение органических полимеров, изд. «Мир», М., 1967, стр. 208.
17. Shindo, Kobunshi, 11, 11 (1962).
18. В. А. Каргин, И. А. Литвинов, Высокомолек. соед., 7, 226 (1965).
19. Пат. США № 3855696, 1966.
20. Франц. пат. № 1430903, 1966.
21. Пат. США № 3179605, 1964; № 3290489, 1967.
22. О. П. Голова и др., Высокомолек. соед., 1, 1295 (1959); ДАН СССР, 116, 419 (1957); 115, 1122 (1957); 112, 430 (1957); Изв. АН СССР, ОХН, 1957, 1499; 1957, 389.
23. O. Vobeer, E. Sperk, Ber. Deutsch. keram. Gesellschaft, B 43, 199 (1966); Франц. пат. № 1462564, 1966; № 1524502, 1968; D. Schmidt, W. Jones, Chem. Eng. Progr., 58, 42 (1962); Пат. США № 3235329, 1966; № 3305315, 1967; Англ. пат. № 179324, 1970; № 1033009, 1968; Пат. ФРГ № 1242551, 1967.
24. F. Kilzer, A. Broido, Pyrodinamica, 2, 151 (1965).
25. S. Rosa, Text. Res. J., 38, 906 (1968).
26. M. Tang, R. Bacon, Carbon, 2, 211 (1964).
27. N. Losty, N. Blacklock, Second Conf. Ind. Carbon a. Graphite, London, April, 1965.
28. А. С. Филалков и др., Хим. твердого топлива, № 3, 116 (1968).

29. В. Е. Котина, А. А. Конкин, В. О. Горбачева, Н. Ф. Ерофеева, Хим. волокна, № 6, 1 (1969).
30. Англ. пат. № 894458, 1962; Пат. США № 3116975, 1964.
31. Франц. пат. № 1406529, 1965.
32. W. Gibson, G. Langlois, Polymer Preprints, 9, 1376 (1968).
33. R. Vason, W. Schalamon, ibid., 9, 285 (1968).
34. Изеккил, Спейн, в сб. «Новое в производстве химических волокон», изд. «Мир», 1968, стр. 169; Пат. ФРГ № 1226925; Франц. пат. № 1538887, 1968.
35. Пат. ФРГ № 1246510, 1968; Пат. США № 3427120, 1969.
36. A. Shindo, J. Nakanish, J. Soma, Appl. Polymer Symposia, 9, 305 (1969).
37. Англ. пат. № 1166251, 1969.
38. Пат. США № 3528774, 1970.
39. S. Otani, J. Soc. Chem. Ind. Japan, 61, 447 (1958); S. Otani, ibid., 61, 1324 (1958); S. Otani, T. Ichikawa, J. Chem. Soc. Japan, 65, 1617 (1962).
40. S. Otani, Carbon, 3, 31 (1965).
41. Rubb. Plast. Age, 80, 328 (1969).
42. S. Otani e. a., Carbon, 4, 425 (1966).
43. H. Hawtherne, C. Baker, R. Bental, K. Linder, Nature, 227, 946 (1970); H. Hawtherne, Inter. Conf. on Carbon Fibres their Composites a. Applic., London, 1971, paper № 13.
44. S. Otani, Carbon, 3, 213 (1965).
45. Франц. пат. № 2019821, 1970.
46. S. Jamado, M. Yamamoto, Appl. Polymer Symposia, 9, 359 (1969).
47. J. Economy, J. Materials Sci., 6, 1151 (1971).
48. Ямада Качаку, Соти, 5, 61 (1963), пер. ВИНТИ.
48. Швейц. пат. № 514500, 1971.
50. Chem. Eng., 72, 29 (1965); Mater Eng., 67, 94 (1968); ibid., 68, 49 (1968); J. Compos. Materials., 3, 684 (1969); Prod. Eng., 41, 14, 10 (1971).
51. Reinf. Plast., 14, 132 (1970); Plast. Rubb. Text., 1, 62 (1970); The Eng., 228, 20 (1969); Mol. Ind., 88, 22 (1970); New. Sci., 41, 398 (1969).
52. Shindo, Bull. Osaka Juastr. Inst., 12, 110 (1961).
53. Л. Браутман, Р. Крок, Современные композиционные материалы, изд. «Мир», 1970, стр. 315; N. Judd, Inter. Conf. on Carbon Fibres their Composites a. Applic., London, 1971, paper № 32; J. Rav, ibid., paper № 29, D. Robbins, ibid., paper № 30.